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NONAQUEOUS DETERGENT COMPOSITIONS CONTAINING SPECIFIC ALKYL BENZENE SULFONATE SURFACTANT

FIELD OF THE INVENTION

This invention relates to liquid laundry detergent products which are nonaqueous in nature and which are in the form of stable dispersions of particulate material such as bleaching agents and/or other detergent composition adjuvants.

BACKGROUND OF THE INVENTION

Liquid nonaqueous detergents are well known in the art. This class of detergents is particularly interesting for enhancing the chemical compatibility of detergent composition components, in particular bleaching agents.

In such nonaqueous products, at least some of the normally solid detergent composition components tend to be less reactive with each other than if they had been dissolved in the aqueous liquid matrix.

Even though chemical compatibility of components may be enhanced in nonaqueous liquid detergent compositions, physical stability of such compositions may become a problem. This is because there is a tendency for such products to phase separate as dispersed insoluble solid particulate material drops from suspension and settles at the bottom of the container holding the liquid detergent product. As one consequence of this type of problem, there can also be difficulties associated with incorporating enough of the right types and amounts of surfactants, in particular anionic surfactants, into nonaqueous liquid detergent products. Anionic surfactants must, of course, be selected such that they are suitable for imparting acceptable fabric cleaning performance to such compositions but utilization of such materials must not lead to an unacceptable degree of viscosity increase. Viscosity control agents can be added to such products to improve the physical stability thereof. Such materials, however, can add cost and bulk to the product without contributing to the laundering/cleaning performance of such detergent compositions.

Given the foregoing, there is clearly a continuing need to identify and provide liquid, anionic-containing detergent compositions in the form of nonaqueous liquid products that have a high degree of physical stability along with commercially acceptable pourability. Accordingly, it is an object of the present invention to provide nonaqueous, anionic-containing liquid detergent products which have such especially desirable physical stability characteristics as well as outstanding pourability characteristics.

Nonaqueous liquid detergent compositions containing high level of anionic surfactants are described in DE 3 728 047, EP 484 095 and WO 92/09678. None of the art teaches, discloses or suggests that selectivity of the alkylbenzene sulfonates result in a liquid nonaqueous detergent

composition with excellent physical and pourability characteristics.

#### SUMMARY of the INVENTION

The present invention provides nonaqueous liquid detergent compositions comprising an anionic surfactant selected from the alkali metal salts of C<sub>10</sub>-C<sub>16</sub> alkylbenzene sulfonic acids derived from alkylbenzenes having tetraline content lower than 5%.

#### DETAILED DESCRIPTION of the INVENTION

##### (A) Essential Anionic Surfactant

The anionic surfactant essentially utilized as an essential component of the nonaqueous liquid phase is one selected from the alkali metal salts of alkylbenzene sulfonic acids in which the alkyl group contains from about 10 to 16 carbon atoms, in straight chain or branched chain configuration characterized in that the tetraline content of the alkylbenzene sulfonic acid is less than 10%, preferably less than 5%. Tetraline is a byproduct as a result of the production of linear alkyl benzenes.

Especially preferred are the sodium and potassium linear straight chain alkylbenzene sulfonates (LAS) in which the average number of carbon atoms in the alkyl group is from about 11 to 14. Sodium C<sub>11</sub>-C<sub>14</sub> LAS is especially preferred.

The alkylbenzene sulfonate anionic surfactant will be partially dissolved in the nonaqueous liquid diluent. To form the structured liquid phase required for suitable phase stability and acceptable rheology, the alkylbenzene sulfonate anionic surfactant is generally present to the extent of from about 30% to 65% by weight of the liquid phase. More preferably, the alkylbenzene sulfonate anionic

surfactant will comprise from about 35% to 50% by weight of the nonaqueous liquid phase of the compositions herein. Utilization of this anionic surfactant in these concentrations corresponds to an anionic surfactant concentration in the total composition of from about 15% to 60% by weight, more preferably from about 20% to 40% by weight of the composition.

(B) The nonaqueous detergent composition of this invention may further comprise a surfactant- and low-polarity solvent-containing liquid phase having dispersed therein the alkyl benzene sulfonic acid. The components of the liquid and solid phases of the detergent compositions herein, as well as composition form, preparation and use, are described in greater detail as follows :  
All concentrations and ratios are on a weight basis unless otherwise specified.

#### Additional Surfactant

The amount of the surfactant mixture component of the detergent compositions herein can vary depending upon the nature and amount of other composition components and depending upon the desired rheological properties of the ultimately formed composition. Generally, this surfactant mixture will be used in an amount comprising from about 10% to 90% by weight of the composition. More preferably, the surfactant mixture will comprise from about 15% to 50% by weight of the composition.

A typical listing of anionic, nonionic, amphotolytic and zwitterionic classes, and species of these surfactants, is given in US Patent 3,664,961 issued to Norris on May 23, 1972.

Preferred anionic surfactants include the alkyl sulfate surfactants hereof are water soluble salts or acids

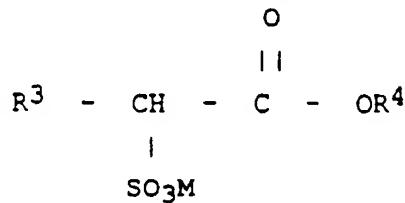
of the formula  $ROSO_3M$  wherein R preferably is a C<sub>10</sub>-C<sub>24</sub> hydrocarbyl, preferably an alkyl or hydroxyalkyl having a C<sub>10</sub>-C<sub>18</sub> alkyl component, more preferably a C<sub>12</sub>-C<sub>15</sub> alkyl or hydroxyalkyl, and M is H or a cation, e.g., an alkali metal cation (e.g. sodium, potassium, lithium), or ammonium or substituted ammonium (quaternary ammonium cations such as tetramethyl-ammonium and dimethyl piperdinium cations).

Highly preferred anionic surfactants include alkyl alkoxylated sulfate surfactants hereof are water soluble salts or acids of the formula  $RO(A)_mSO_3M$  wherein R is an unsubstituted C<sub>10</sub>-C<sub>24</sub> alkyl or hydroxyalkyl group having a C<sub>10</sub>-C<sub>24</sub> alkyl component, preferably a C<sub>12</sub>-C<sub>18</sub> alkyl or hydroxyalkyl, A is an ethoxy or propoxy unit, m is greater than zero, typically between about 0.5 and about 6, more preferably between about 0.5 and about 3, and M is H or a cation which can be, for example, a metal cation (e.g., sodium, potassium, lithium, calcium, magnesium, etc.), ammonium or substituted-ammonium cation. Alkyl ethoxylated sulfates as well as alkyl propoxylated sulfates are contemplated herein. Specific examples of substituted ammonium cations include quaternary ammonium cations such as tetramethyl-ammonium and dimethyl piperdinium cations. Exemplary surfactants are C<sub>12</sub>-C<sub>15</sub> alkyl polyethoxylate (1.0) sulfate (C<sub>12</sub>-C<sub>15</sub>E(1.0)M), C<sub>12</sub>-C<sub>15</sub> alkyl polyethoxylate (2.25) sulfate (C<sub>12</sub>-C<sub>15</sub>E(2.25)M), C<sub>12</sub>-C<sub>15</sub> alkyl polyethoxylate (3.0) sulfate (C<sub>12</sub>-C<sub>15</sub>E(3.0)M), and C<sub>12</sub>-C<sub>15</sub> alkyl polyethoxylate (4.0) sulfate (C<sub>12</sub>-C<sub>15</sub>E(4.0)M), wherein M is conveniently selected from sodium and potassium.

Other suitable anionic surfactants to be used are alkyl ester sulfonate surfactants including linear esters of C<sub>8</sub>-C<sub>20</sub> carboxylic acids (i.e., fatty acids) which are sulfonated with gaseous SO<sub>3</sub> according to "The Journal of the American Oil Chemists Society", 52 (1975), pp. 323-329.

Suitable starting materials would include natural fatty substances as derived from tallow, palm oil, etc.

The preferred alkyl ester sulfonate surfactant, especially for laundry applications, comprise alkyl ester sulfonate surfactants of the structural formula :



wherein  $\text{R}^3$  is a  $\text{C}_8\text{-C}_{20}$  hydrocarbyl, preferably an alkyl, or combination thereof,  $\text{R}^4$  is a  $\text{C}_1\text{-C}_6$  hydrocarbyl, preferably an alkyl, or combination thereof, and M is a cation which forms a water soluble salt with the alkyl ester sulfonate. Suitable salt-forming cations include metals such as sodium, potassium, and lithium, and substituted or unsubstituted ammonium cations. Preferably,  $\text{R}^3$  is  $\text{C}_{10}\text{-C}_{16}$  alkyl, and  $\text{R}^4$  is methyl, ethyl or isopropyl. Especially preferred are the methyl ester sulfonates wherein  $\text{R}^3$  is  $\text{C}_{10}\text{-C}_{16}$  alkyl.

Other anionic surfactants useful for detergents purposes can also be included in the laundry detergent compositions of the present invention. These can include salts (including, for example, sodium, potassium, ammonium, and substituted ammonium salts such as mono-, di- and triethanolamine salts) of soap,  $\text{C}_8\text{-C}_{22}$  primary or secondary alkanesulfonates,  $\text{C}_8\text{-C}_{24}$  olefinsulfonates, sulfonated polycarboxylic acids prepared by sulfonation of the pyrolyzed product of alkaline earth metal citrates, e.g., as described in British patent specification No. 1,082,179,  $\text{C}_8\text{-C}_{24}$  alkylpolyglycolethersulfates (containing up to 10 moles of ethylene oxide); alkyl glycerol sulfonates, fatty acyl glycerol sulfonates, fatty oleyl glycerol sulfates, alkyl phenol ethylene oxide ether sulfates, paraffin sulfonates, alkyl phosphates, isethionates such as the acyl isethionates, N-acyl taurates, alkyl succinamates and sulfosuccinates, monoesters of sulfosuccinates (especially

saturated and unsaturated C<sub>12</sub>-C<sub>18</sub> monoesters) and diesters of sulfosuccinates (especially saturated and unsaturated C<sub>6</sub>-C<sub>12</sub> diesters), sulfates of alkylpolysaccharides such as the sulfates of alkylpolyglucoside (the nonionic nonsulfated compounds being described below), and alkyl polyethoxy carboxylates such as those of the formula RO(CH<sub>2</sub>CH<sub>2</sub>O)<sub>k</sub>-CH<sub>2</sub>COO-M<sup>+</sup> wherein R is a C<sub>8</sub>-C<sub>22</sub> alkyl, k is an integer from 1 to 10, and M is a soluble salt-forming cation. Resin acids and hydrogenated resin acids are also suitable, such as rosin, hydrogenated rosin, and resin acids and hydrogenated resin acids present in or derived from tall oil. Further examples are described in "Surface Active Agents and Detergents" (Vol. I and II by Schwartz, Perry and Berch). A variety of such surfactants are also generally disclosed in U.S. Patent 3,929,678, issued December 30, 1975 to Laughlin, et al. at Column 23, line 58 through Column 29, line 23 (herein incorporated by reference).

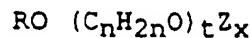
When included therein, the detergent compositions of the present invention typically comprise from about 1% to about 40%, preferably from about 5% to about 25% by weight of such anionic surfactants.

One class of nonionic surfactants useful in the present invention are condensates of ethylene oxide with a hydrophobic moiety to provide a surfactant having an average hydrophilic-lipophilic balance (HLB) in the range from 8 to 17, preferably from 9.5 to 14, more preferably from 12 to 14. The hydrophobic (lipophilic) moiety may be aliphatic or aromatic in nature and the length of the polyoxyethylene group which is condensed with any particular hydrophobic group can be readily adjusted to yield a water-soluble compound having the desired degree of balance between hydrophilic and hydrophobic elements.

Especially preferred nonionic surfactants of this type are the C<sub>9</sub>-C<sub>15</sub> primary alcohol ethoxylates containing 3-12

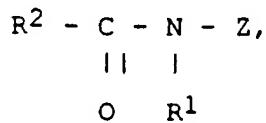
moles of ethylene oxide per mole of alcohol, particularly the C<sub>12</sub>-C<sub>15</sub> primary alcohols containing 5-8 moles of ethylene oxide per mole of alcohol.

Another class of nonionic surfactants comprises alkyl polyglucoside compounds of general formula



wherein Z is a moiety derived from glucose; R is a saturated hydrophobic alkyl group that contains from 12 to 18 carbon atoms; t is from 0 to 10 and n is 2 or 3; x is from 1.3 to 4, the compounds including less than 10% unreacted fatty alcohol and less than 50% short chain alkyl polyglucosides. Compounds of this type and their use in detergent are disclosed in EP-B 0 070 077, 0 075 996 and 0 094 118.

Also suitable as nonionic surfactants are poly hydroxy fatty acid amide surfactants of the formula



wherein R<sup>1</sup> is H, or R<sup>1</sup> is C<sub>1</sub>-4 hydrocarbyl, 2-hydroxy ethyl, 2-hydroxy propyl or a mixture thereof, R<sup>2</sup> is C<sub>5</sub>-31 hydrocarbyl, and Z is a polyhydroxyhydrocarbyl having a linear hydrocarbyl chain with at least 3 hydroxyls directly connected to the chain, or an alkoxylated derivative thereof. Preferably, R<sup>1</sup> is methyl, R<sup>2</sup> is a straight C<sub>11</sub>-15 alkyl or alkenyl chain such as coconut alkyl or mixtures thereof, and Z is derived from a reducing sugar such as glucose, fructose, maltose, lactose, in a reductive amination reaction.

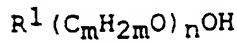
#### Nonaqueous Liquid Diluent

To form the liquid phase of the detergent compositions, the hereinbefore described surfactant (mixture) may be

combined with a nonaqueous liquid diluent such as a liquid alcohol alkoxylate material or a nonaqueous, low-polarity organic solvent.

#### Alcohol Alkoxylates

One component of the liquid diluent suitable to form the compositions herein comprises an alkoxylated fatty alcohol material. Such materials are themselves also nonionic surfactants. Such materials correspond to the general formula:



wherein  $R^1$  is a  $C_8 - C_{16}$  alkyl group,  $m$  is from 2 to 4, and  $n$  ranges from about 2 to 12. Preferably  $R^1$  is an alkyl group, which may be primary or secondary, that contains from about 9 to 15 carbon atoms, more preferably from about 10 to 14 carbon atoms. Preferably also the alkoxylated fatty alcohols will be ethoxylated materials that contain from about 2 to 12 ethylene oxide moieties per molecule, more preferably from about 3 to 10 ethylene oxide moieties per molecule.

The alkoxylated fatty alcohol component of the liquid diluent will frequently have a hydrophilic-lipophilic balance (HLB) which ranges from about 3 to 17. More preferably, the HLB of this material will range from about 6 to 15, most preferably from about 8 to 15.

Examples of fatty alcohol alkoxylates useful as one of the essential components of the nonaqueous liquid diluent in the compositions herein will include those which are made from alcohols of 12 to 15 carbon atoms and which contain about 7 moles of ethylene oxide. Such materials have been commercially marketed under the trade names Neodol 25-7 and Neodol 23-6.5 by Shell Chemical Company. Other useful Neodols include Neodol 1-5, an ethoxylated fatty alcohol averaging 11 carbon atoms in its alkyl chain with about 5 moles of ethylene oxide; Neodol 23-9, an

ethoxylated primary C<sub>12</sub> - C<sub>13</sub> alcohol having about 9 moles of ethylene oxide and Neodol 91-10, an ethoxylated C<sub>9</sub> - C<sub>11</sub> primary alcohol having about 10 moles of ethylene oxide. Alcohol ethoxylates of this type have also been marketed by Shell Chemical Company under the Dobanol trademark. Dobanol 91-5 is an ethoxylated C<sub>9</sub>-C<sub>11</sub> fatty alcohol with an average of 5 moles ethylene oxide and Dobanol 25-7 is an ethoxylated C<sub>12</sub>-C<sub>15</sub> fatty alcohol with an average of 7 moles of ethylene oxide per mole of fatty alcohol.

Other examples of suitable ethoxylated alcohols include Tergitol 15-S-7 and Tergitol 15-S-9 both of which are linear secondary alcohol ethoxylates that have been commercially marketed by Union Carbide Corporation. The former is a mixed ethoxylation product of C<sub>11</sub> to C<sub>15</sub> linear secondary alkanol with 7 moles of ethylene oxide and the latter is a similar product but with 9 moles of ethylene oxide being reacted.

Other types of alcohol ethoxylates useful in the present compositions are higher molecular weight nonionics, such as Neodol 45-11, which are similar ethylene oxide condensation products of higher fatty alcohols, with the higher fatty alcohol being of 14-15 carbon atoms and the number of ethylene oxide groups per mole being about 11. Such products have also been commercially marketed by Shell Chemical Company.

The alcohol alkoxylate component when utilized as part of the liquid diluent in the nonaqueous compositions herein will generally be present to the extent of from about 1% to 60% by weight of the composition. More preferably, the alcohol alkoxylate component will comprise about 5% to 40% by weight of the compositions herein. Most preferably, the alcohol alkoxylate component will comprise from about 10% to 25% by weight of the detergent compositions herein.

Nonaqueous Low-Polarity Organic Solvent

Another component of the liquid diluent which may form part of the detergent compositions herein comprises nonaqueous, low-polarity organic solvent(s). The term "solvent" is used herein to connote the non-surface active carrier or diluent portion of the liquid phase of the composition. While some of the essential and/or optional components of the compositions herein may actually dissolve in the "solvent"-containing phase, other components will be present as particulate material dispersed within the "solvent"-containing phase. Thus the term "solvent" is not meant to require that the solvent material be capable of actually dissolving all of the detergent composition components added thereto.

The nonaqueous organic materials which are employed as solvents herein are those which are liquids of low polarity. For purposes of this invention, "low-polarity" liquids are those which have little, if any, tendency to dissolve one of the preferred types of particulate material used in the compositions herein, i.e., the peroxygen bleaching agents, sodium perborate or sodium percarbonate. Thus relatively polar solvents such as ethanol should not be utilized. Suitable types of low-polarity solvents useful in the nonaqueous liquid detergent compositions herein do include alkylene glycol mono lower alkyl ethers, lower molecular weight polyethylene glycols, lower molecular weight methyl esters and amides, and the like.

A preferred type of nonaqueous, low-polarity solvent for use herein comprises the mono-, di-, tri-, or tetra- $C_2-C_3$  alkylene glycol mono  $C_2-C_6$  alkyl ethers. The specific examples of such compounds include diethylene glycol monobutyl ether, tetraethylene glycol monobutyl ether, dipropylene glycol monoethyl ether, and dipropylene glycol monobutyl ether. Diethylene glycol monobutyl ether and dipropylene glycol monobutyl ether are especially preferred. Compounds of the type have been commercially

marketed under the tradenames Dowanol, Carbitol, and Cellosolve.

Another preferred type of nonaqueous, low-polarity organic solvent useful herein comprises the lower molecular weight polyethylene glycols (PEGs). Such materials are those having molecular weights of at least about 150. PEGs of molecular weight ranging from about 200 to 600 are most preferred.

Yet another preferred type of non-polar, nonaqueous solvent comprises lower molecular weight methyl esters. Such materials are those of the general formula:  $R^1-C(O)-OCH_3$  wherein  $R^1$  ranges from 1 to about 18. Examples of suitable lower molecular weight methyl esters include methyl acetate, methyl propionate, methyl octanoate, and methyl dodecanoate.

The nonaqueous, low-polarity organic solvent(s) employed should, of course, be compatible and non-reactive with other composition components, e.g., bleach and/or activators, used in the liquid detergent compositions herein. Such a solvent component will generally be utilized in an amount of from about 1% to 60% by weight of the composition. More preferably, the nonaqueous, low-polarity organic solvent will comprise from about 5% to 40% by weight of the composition, most preferably from about 10% to 25% by weight of the composition.

#### Liquid Diluent Concentration

As with the concentration of the surfactant mixture, the amount of total liquid diluent in the compositions herein will be determined by the type and amounts of other composition components and by the desired composition properties. Generally, the liquid diluent will comprise from about 20% to 95% by weight of the compositions herein. More preferably, the liquid diluent will comprise from about 50% to 70% by weight of the composition.

SOLID PHASE

The nonaqueous detergent compositions herein may further comprise a solid phase of particulate material which is dispersed and suspended within the liquid phase. Generally such particulate material will range in size from about 0.1 to 1500 microns. More preferably such material will range in size from about 5 to 500 microns.

The particulate material utilized herein can comprise one or more types of detergent composition components which in particulate form are substantially insoluble in the nonaqueous liquid phase of the composition. The types of particulate materials which can be utilized are described in detail as follows:

Peroxygen Bleaching Agent With Optional Bleach Activators

The most preferred type of particulate material useful for forming the solid phase of the detergent compositions herein comprises particles of a peroxygen bleaching agent. Such peroxygen bleaching agents may be organic or inorganic in nature. Inorganic peroxygen bleaching agents are frequently utilized in combination with a bleach activator.

Useful organic peroxygen bleaching agents include percarboxylic acid bleaching agents and salts thereof. Suitable examples of this class of agents include magnesium monoperoxyphthalate hexahydrate, the magnesium salt of metachloro perbenzoic acid, 4-nonylamino-4-oxoperoxybutyric acid and diperoxydodecanedioic acid. Such bleaching agents are disclosed in U.S. Patent 4,483,781, Hartman, Issued November 20, 1984; European Patent Application EP-A-133,354, Banks et al., Published February 20, 1985; and U.S. Patent 4,412,934, Chung et al., Issued November 1, 1983. Highly preferred bleaching agents also include 6-nonylamino-6-oxoperoxycaproic acid (NAPAA) as described in U.S. Patent 4,634,551, Issued January 6, 1987 to Burns et al.

Inorganic peroxygen bleaching agents may also be used in particulate form in the detergent compositions herein. Inorganic bleaching agents are in fact preferred. Such inorganic peroxygen compounds include alkali metal perborate and percarbonate materials, most preferably the percarbonates. For example, sodium perborate (e.g. mono- or tetra-hydrate) can be used. Suitable inorganic bleaching agents can also include sodium or potassium carbonate peroxyhydrate and equivalent "percarbonate" bleaches, sodium pyrophosphate peroxyhydrate, urea peroxyhydrate, and sodium peroxide. Persulfate bleach (e.g., OXONE, manufactured commercially by DuPont) can also be used. Frequently inorganic peroxygen bleaches will be coated with silicate, borate, sulfate or water-soluble surfactants. For example, coated percarbonate particles are available from various commercial sources such as FMC, Solvay Interox, Tokai Denka and Degussa.

Inorganic peroxygen bleaching agents, e.g., the perborates, the percarbonates, etc., are preferably combined with bleach activators, which lead to the *in situ* production in aqueous solution (i.e., during use of the compositions herein for fabric laundering/bleaching) of the peroxy acid corresponding to the bleach activator. Various non-limiting examples of activators are disclosed in U.S. Patent 4,915,854, Issued April 10, 1990 to Mao et al.; and U.S. Patent 4,412,934 Issued November 1, 1983 to Chung et al. The nonanoyloxybenzene sulfonate (NOBS) and tetraacetyl ethylene diamine (TAED) activators are typical. Mixtures thereof can also be used. See also the hereinbefore referenced U.S. 4,634,551 for other typical bleaches and activators useful herein.

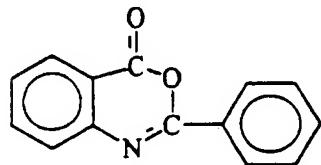
Other useful amido-derived bleach activators are those of the formulae:



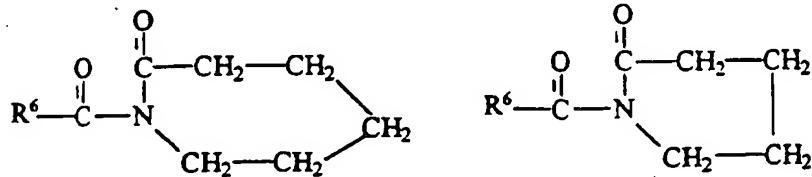
wherein R<sup>1</sup> is an alkyl group containing from about 6 to about 12 carbon atoms, R<sup>2</sup> is an alkylene containing from 1 to about 6 carbon atoms, R<sup>5</sup> is H or alkyl, aryl, or alkaryl containing from about 1 to about 10 carbon atoms, and L is any suitable leaving group. A leaving group is any group that is displaced from the bleach activator as a consequence of the nucleophilic attack on the bleach activator by the perhydrolysis anion. A preferred leaving group is phenol sulfonate.

Preferred examples of bleach activators of the above formulae include (6-octanamido-caproyl)oxybenzenesulfonate, (6-nonenamido-caproyl) oxybenzenesulfonate, (6-decanamido-caproyl)oxybenzenesulfonate and mixtures thereof as described in the hereinbefore referenced U.S. Patent 4,634,551. Such mixtures are characterized herein as (6-C<sub>8</sub>-C<sub>10</sub> alkamido-caproyl)oxybenzenesulfonate.

Another class of useful bleach activators comprises the benzoxazin-type activators disclosed by Hodge et al. in U.S. Patent 4,966, 723, Issued October 30, 1990, incorporated herein by reference. A highly preferred activator of the benzoxazin-type is:



Still another class of useful bleach activators includes the acyl lactam activators, especially acyl caprolactams and acyl valerolactams of the formulae:



wherein R<sup>6</sup> is H or an alkyl, aryl, alkoxyaryl, or alkaryl group containing from 1 to about 12 carbon atoms. Highly preferred lactam activators include benzoyl caprolactam, octanoyl caprolactam, 3,5,5-trimethylhexanoyl caprolactam,

nonanoyl caprolactam, decanoyl caprolactam, undecenoyl caprolactam, benzoyl valerolactam, octanoyl valerolactam, decanoyl valerolactam, undecenoyl valerolactam, 3,5,5-trimethylhexanoyl valerolactam and mixtures thereof. See also U.S. Patent 4,545,784, Issued to Sanderson, October 8, 1985, incorporated herein by reference, which discloses acyl caprolactams, including benzoyl caprolactam, adsorbed into sodium perborate.

If peroxygen bleaching agents are used as all or part of the essentially present particulate material, they will generally comprise from about 1% to 30% by weight of the composition. More preferably, peroxygen bleaching agent will comprise from about 1% to 20% by weight of the composition. Most preferably, peroxygen bleaching agent will be present to the extent of from about 3% to 15% by weight of the composition. If utilized, bleach activators can comprise from about 0.5% to 20%, more preferably from about 1% to 10%, by weight of the composition. Frequently, activators are employed such that the molar ratio of bleaching agent to activator ranges from about 1:1 to 10:1, more preferably from about 1.5:1 to 5:1.

In addition, it has been found that bleach activators, when agglomerated with certain acids such as citric acid, are more chemically stable.

### Surfactants

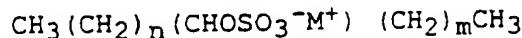
Another possible type of particulate material which can be suspended in the nonaqueous liquid detergent compositions herein includes ancillary anionic surfactants which are fully or partially insoluble in the nonaqueous liquid phase. The most common type of anionic surfactant with such solubility properties comprises primary or secondary alkyl sulfate anionic surfactants. Such surfactants are those produced by the sulfation of higher C<sub>8</sub>-C<sub>20</sub> fatty alcohols.

Conventional primary alkyl sulfate surfactants have the general formula



wherein R is typically a linear C<sub>8</sub> - C<sub>20</sub> hydrocarbyl group, which may be straight chain or branched chain, and M is a water-solubilizing cation. Preferably R is a C<sub>10</sub> - C<sub>14</sub> alkyl, and M is alkali metal. Most preferably R is about C<sub>12</sub> and M is sodium.

Conventional secondary alkyl sulfates may also be utilized as the essential anionic surfactant component of the solid phase of the compositions herein. Conventional secondary alkyl sulfate surfactants are those materials which have the sulfate moiety distributed randomly along the hydrocarbyl "backbone" of the molecule. Such materials may be depicted by the structure



wherein m and n are integers of 2 or greater and the sum of m + n is typically about 9 to 15, and M is a water-solubilizing cation.

If utilized as all or part of the requisite particulate material, ancillary anionic surfactants such as alkyl sulfates will generally comprise from about 1% to 10% by weight of the composition, more preferably from about 1% to 5% by weight of the composition. Alkyl sulfate used as all or part of the particulate material is prepared and added to the compositions herein separately from the unalkoxylated alkyl sulfate material which may form part of the alkyl ether sulfate surfactant component essentially utilized as part of the liquid phase herein.

#### Organic Builder Material

Another possible type of particulate material which can be suspended in the nonaqueous liquid detergent

compositions herein comprises an organic detergent builder material which serves to counteract the effects of calcium, or other ion, water hardness encountered during laundering/bleaching use of the compositions herein. Examples of such materials include the alkali metal, citrates, succinates, malonates, fatty acids, carboxymethyl succinates, carboxylates, polycarboxylates and polyacetyl carboxylates. Specific examples include sodium, potassium and lithium salts of oxydisuccinic acid, mellitic acid, benzene polycarboxylic acids and citric acid. Other examples of organic phosphonate type sequestering agents such as those which have been sold by Monsanto under the Dequest tradename and alkanehydroxy phosphonates. Citrate salts are highly preferred.

Other suitable organic builders include the higher molecular weight polymers and copolymers known to have builder properties. For example, such materials include appropriate polyacrylic acid, polymaleic acid, and polyacrylic/polymaleic acid copolymers and their salts, such as those sold by BASF under the Sokalan trademark.

Another suitable type of organic builder comprises the water-soluble salts of higher fatty acids, i.e., "soaps". These include alkali metal soaps such as the sodium, potassium, ammonium, and alkylolammonium salts of higher fatty acids containing from about 8 to about 24 carbon atoms, and preferably from about 12 to about 18 carbon atoms. Soaps can be made by direct saponification of fats and oils or by the neutralization of free fatty acids. Particularly useful are the sodium and potassium salts of the mixtures of fatty acids derived from coconut oil and tallow, i.e., sodium or potassium tallow and coconut soap.

If utilized as all or part of the requisite particulate material, insoluble organic detergent builders can generally comprise from about 1% to 20% by weight of the compositions herein. More preferably, such builder material can comprise from about 4% to 10% by weight of the composition.

Inorganic Alkalinity Sources

Another possible type of particulate material which can be suspended in the nonaqueous liquid detergent compositions herein can comprise a material which serves to render aqueous washing solutions formed from such compositions generally alkaline in nature. Such materials may or may not also act as detergent builders, i.e., as materials which counteract the adverse effect of water hardness on detergency performance.

Examples of suitable alkalinity sources include water-soluble alkali metal carbonates, bicarbonates, borates, silicates and metasilicates. Although not preferred for ecological reasons, water-soluble phosphate salts may also be utilized as alkalinity sources. These include alkali metal pyrophosphates, orthophosphates, polyphosphates and phosphonates. Of all of these alkalinity sources, alkali metal carbonates such as sodium carbonate are the most preferred.

The alkalinity source, if in the form of a hydratable salt, may also serve as a desiccant in the nonaqueous liquid detergent compositions herein. The presence of an alkalinity source which is also a desiccant may provide benefits in terms of chemically stabilizing those composition components such as the peroxygen bleaching agent which may be susceptible to deactivation by water.

If utilized as all or part of the particulate material component, the alkalinity source will generally comprise from about 1% to 15% by weight of the compositions herein. More preferably, the alkalinity source can comprise from about 2% to 10% by weight of the composition. Such materials, while water-soluble, will generally be insoluble in the nonaqueous detergent compositions herein. Thus such materials will generally be dispersed in the nonaqueous liquid phase in the form of discrete particles.

OPTIONAL COMPOSITION COMPONENTS

In addition to the composition liquid and solid phase components as hereinbefore described, the detergent compositions herein can, and preferably will, contain various optional components. Such optional components may be in either liquid or solid form. The optional components may either dissolve in the liquid phase or may be dispersed within the liquid phase in the form of fine particles or droplets. Some of the materials which may optionally be utilized in the compositions herein are described in greater detail as follows:

Optional Inorganic Detergent Builders

The detergent compositions herein may also optionally contain one or more types of inorganic detergent builders beyond those listed hereinbefore that also function as alkalinity sources. Such optional inorganic builders can include, for example, aluminosilicates such as zeolites. Aluminosilicate zeolites, and their use as detergent builders are more fully discussed in Corkill et al., U.S. Patent No. 4,605,509; Issued August 12, 1986, the disclosure of which is incorporated herein by reference. Also crystalline layered silicates, such as those discussed in this '509 U.S. patent, are also suitable for use in the detergent compositions herein. If utilized, optional inorganic detergent builders can comprise from about 2% to 15% by weight of the compositions herein.

Optional Enzymes

The detergent compositions herein may also optionally contain one or more types of detergent enzymes. Such enzymes can include proteases, amylases, cellulases and lipases. Such materials are known in the art and are commercially available. They may be incorporated into the

nonaqueous liquid detergent compositions herein in the form of suspensions, "marumes" or "prills". Another suitable type of enzyme comprises those in the form of slurries of enzymes in nonionic surfactants. Enzymes in this form have been commercially marketed, for example, by Novo Nordisk under the tradename "LDP."

Enzymes added to the compositions herein in the form of conventional enzyme prills are especially preferred for use herein. Such prills will generally range in size from about 100 to 1,000 microns, more preferably from about 200 to 800 microns and will be suspended throughout the nonaqueous liquid phase of the composition. Prills in the compositions of the present invention have been found, in comparison with other enzyme forms, to exhibit especially desirable enzyme stability in terms of retention of enzymatic activity over time. Thus, compositions which utilize enzyme prills need not contain conventional enzyme stabilizing such as must frequently be used when enzymes are incorporated into aqueous liquid detergents.

If employed, enzymes will normally be incorporated into the nonaqueous liquid compositions herein at levels sufficient to provide up to about 10 mg by weight, more typically from about 0.01 mg to about 5 mg, of active enzyme per gram of the composition. Stated otherwise, the nonaqueous liquid detergent compositions herein will typically comprise from about 0.001% to 5%, preferably from about 0.01% to 1% by weight, of a commercial enzyme preparation. Protease enzymes, for example, are usually present in such commercial preparations at levels sufficient to provide from 0.005 to 0.1 Anson units (AU) of activity per gram of composition.

#### Optional Chelating Agents

The detergent compositions herein may also optionally contain a chelating agent which serves to chelate metal ions, e.g., iron and/or manganese, within the nonaqueous

detergent compositions herein. Such chelating agents thus serve to form complexes with metal impurities in the composition which would otherwise tend to deactivate composition components such as the peroxygen bleaching agent. Useful chelating agents can include amino carboxylates, phosphonates, amino phosphonates, polyfunctionally-substituted aromatic chelating agents and mixtures thereof.

Amino carboxylates useful as optional chelating agents include ethylenediaminetetraacetates, N-hydroxyethyl-ethylene-diaminetriacetates, nitrilotriacetates, ethylenediamine tetrapropionates, triethylenetetraaminehexacetates, diethylenetriaminepentaacetates, ethylenediaminedisuccinates and ethanoldiglycines. The alkali metal salts of these materials are preferred.

Amino phosphonates are also suitable for use as chelating agents in the compositions of this invention when at least low levels of total phosphorus are permitted in detergent compositions, and include ethylenediaminetetrakis (methylene-phosphonates) as DEQUEST. Preferably, these amino phosphonates do not contain alkyl or alkenyl groups with more than about 6 carbon atoms.

Preferred chelating agents include hydroxyethyl-diphosphonic acid (HEDP), diethylene triamine penta acetic acid (DTPA), ethylenediamine disuccinic acid (EDDS) and dipicolinic acid (DPA) and salts thereof. The chelating agent may, of course, also act as a detergent builder during use of the compositions herein for fabric laundering/ bleaching. The chelating agent, if employed, can comprise from about 0.1% to 4% by weight of the compositions herein. More preferably, the chelating agent will comprise from about 0.2% to 2% by weight of the detergent compositions herein.

Optional Thickening, Viscosity Control and/or Dispersing Agents

The detergent compositions herein may also optionally contain a polymeric material which serves to enhance the ability of the composition to maintain its solid particulate components in suspension. Such materials may thus act as thickeners, viscosity control agents and/or dispersing agents. Such materials are frequently polymeric polycarboxylates but can include other polymeric materials such as polyvinylpyrrolidone (PVP) and polymeric amine derivatives such as quaternized, ethoxylated hexamethylene diamines.

Polymeric polycarboxylate materials can be prepared by polymerizing or copolymerizing suitable unsaturated monomers, preferably in their acid form. Unsaturated monomeric acids that can be polymerized to form suitable polymeric polycarboxylates include acrylic acid, maleic acid (or maleic anhydride), fumaric acid, itaconic acid, aconitic acid, mesaconic acid, citraconic acid and methylenemalonic acid. The presence in the polymeric polycarboxylates herein of monomeric segments, containing no carboxylate radicals such as vinylmethyl ether, styrene, ethylene, etc. is suitable provided that such segments do not constitute more than about 40% by weight of the polymer.

Particularly suitable polymeric polycarboxylates can be derived from acrylic acid. Such acrylic acid-based polymers which are useful herein are the water-soluble salts of polymerized acrylic acid. The average molecular weight of such polymers in the acid form preferably ranges from about 2,000 to 10,000, more preferably from about 4,000 to 7,000, and most preferably from about 4,000 to 5,000. Water-soluble salts of such acrylic acid polymers can include, for example, the alkali metal, salts. Soluble polymers of this type are known materials. Use of polyacrylates of this type in detergent compositions has

been disclosed, for example, Diehl, U.S. Patent 3,308,067, issued March 7, 1967. Such materials may also perform a builder function.

If utilized, the optional thickening, viscosity control and/or dispersing agents should be present in the compositions herein to the extent of from about 0.1% to 4% by weight. More preferably, such materials can comprise from about 0.5% to 2% by weight of the detergents compositions herein.

#### Optional Brighteners, Suds Suppressors and/or Perfumes

The detergent compositions herein may also optionally contain conventional brighteners, suds suppressors, silicone oils, bleach catalysts, and/or perfume materials. Such brighteners, suds suppressors, silicone oils, bleach catalysts, and perfumes must, of course, be compatible and non-reactive with the other composition components in a nonaqueous environment. If present, brighteners suds suppressors and/or perfumes will typically comprise from about 0.01% to 2% by weight of the compositions herein.

Suitable bleach catalysts include the manganese based complexes disclosed in US 5,246,621, US 5,244,594, US 5,114,606 and US 5,114,611.

#### COMPOSITION FORM

The particulate-containing liquid detergent compositions of this invention are substantially nonaqueous (or anhydrous) in character. While very small amounts of water may be incorporated into such compositions as an impurity in the essential or optional components, the amount of water should in no event exceed about 5% by weight of the compositions herein. More preferably, water content of the nonaqueous detergent compositions herein will comprise less than about 1% by weight.

The particulate-containing nonaqueous detergent compositions herein will be in the form of a liquid.

#### COMPOSITION PREPARATION AND USE

The non-aqueous liquid detergent compositions herein can be prepared by first forming the surfactant-containing non-aqueous liquid phase and by thereafter adding to this phase the additional particulate components in any convenient order and by mixing, e.g., agitating, the resulting component combination to form the phase stable compositions herein. In a typical process for preparing such compositions, essential and certain preferred optional components will be combined in a particular order and under certain conditions.

In a first step of a preferred preparation process, the anionic surfactant-containing powder used to form the surfactant-containing liquid phase is prepared. This pre-preparation step involves the formation of an aqueous slurry containing from 40% to 50% of one or more alkali metal salts of linear C<sub>10</sub>-16 alkyl benzene sulfonic acid and from 3% to 15% of one or more diluent non-surfactant salts. In a subsequent step, this slurry is dried to the extent necessary to form a solid material containing less than 5% by weight of residual water.

After preparation of this solid anionic surfactant-containing material, this material can be combined with one or more of the non-aqueous organic solvents to form the surfactant-containing liquid phase of the detergent compositions herein. This is done by reducing the anionic surfactant-containing material formed in the previously described pre-preparation step to powdered form and by combining such powdered material with an agitated liquid medium comprising one or more of the non-aqueous organic solvents, either surfactant or non-surfactant or both, as hereinbefore described. This combination is carried out under agitation conditions which are sufficient to form a

thoroughly mixed dispersion of the LAS/salt material throughout a non-aqueous organic liquid.

In a subsequent processing step, the non-aqueous liquid dispersion so prepared can then be subjected to milling or high shear agitation under conditions which are sufficient to provide the structured, surfactant-containing liquid phase of the detergent compositions herein. Such milling or high shear agitation conditions will generally include maintenance of a temperature between 20°C and 50°C. Milling and high shear agitation of this combination will generally provide an increase in the yield value of the structured liquid phase to within the range of from 1 Pa to 5 Pa.

After formation of the dispersion of LAS/salt co-dried material in the non-aqueous liquid, either before or after such dispersion is milled or agitated to increase its yield value, the additional particulate material to be used in the detergent compositions herein can be added. Such components which can be added under high shear agitation include any optional surfactant particles, particles of substantially all of an organic builder, e.g., citrate and/or fatty acid, and/or an alkalinity source, e.g., sodium carbonate, can be added while continuing to maintain this admixture of composition components under shear agitation. Agitation of the mixture is continued, and if necessary, can be increased at this point to form a uniform dispersion of insoluble solid phase particulates within the liquid phase.

In a second process step, the bleach precursor particles are mixed with the ground suspension from the first mixing step in a second mixing step. This mixture is then subjected to wet grinding so that the average particle size of the bleach precursor is less than 600 microns, preferably between 50 and 500 microns, most preferred between 100 and 400 microns. Other compounds, such as bleach compounds are then added to the resulting mixture.

After some or all of the foregoing solid materials have been added to this agitated mixture, the particles of the highly preferred peroxygen bleaching agent can be added to the composition, again while the mixture is maintained under shear agitation. By adding the peroxygen bleaching agent material last, or after all or most of the other components, and especially after alkalinity source particles, have been added, desirable stability benefits for the peroxygen bleach can be realized. If enzyme prills are incorporated, they are preferably added to the non-aqueous liquid matrix last.

As a final process step, after addition of all of the particulate material, agitation of the mixture is continued for a period of time sufficient to form compositions having the requisite viscosity, yield value and phase stability characteristics. Frequently this will involve agitation for a period of from about 1 to 30 minutes.

In adding solid components to non-aqueous liquids in accordance with the foregoing procedure, it is advantageous to maintain the free, unbound moisture content of these solid materials below certain limits. Free moisture in such solid materials is frequently present at levels of 0.8% or greater. By reducing free moisture content, e.g., by fluid bed drying, of solid particulate materials to a free moisture level of 0.5% or lower prior to their incorporation into the detergent composition matrix, significant stability advantages for the resulting composition can be realized.

The compositions of this invention, prepared as hereinbefore described, can be used to form aqueous washing solutions for use in the laundering and bleaching of fabrics. Generally, an effective amount of such compositions is added to water, preferably in a conventional fabric laundering automatic washing machine, to form such aqueous laundering/bleaching solutions. The aqueous washing/bleaching solution so formed is then

contacted, preferably under agitation, with the fabrics to be laundered and bleached therewith.

An effective amount of the liquid detergent compositions herein added to water to form aqueous laundering/bleaching solutions can comprise amounts sufficient to form from about 500 to 7,000 ppm of composition in aqueous solution. More preferably, from about 800 to 5,000 ppm of the detergent compositions herein will be provided in aqueous washing/bleaching solution.

The following examples illustrate the preparation and performance advantages of non-aqueous liquid detergent compositions of the instant invention. Such examples, however, are not necessarily meant to limit or otherwise define the scope of the invention herein.

EXAMPLE IPreparation of Non-Aqueous Liquid Detergent Composition

- 1) Butoxy-propoxy-propanol (BPP) and a C<sub>12</sub>-16EO(5) ethoxylated alcohol nonionic surfactant (Genapol 24/50) are mixed for a short time (1-5 minutes) using a blade impeller in a mix tank into a single phase.
- 2) NaLAS is added to the BPP/Genapol solution in the mix tank to partially dissolve the NaLAS. Mix time is approximately one hour. The tank is blanketed with nitrogen to prevent moisture pickup from the air.
- 3) If needed, liquid base (LAS/BPP/NI) is pumped out into drums. Molecular sieves (type 3A, 4-8 mesh) are added to each drum at 10% of the net weight of the liquid base. The molecular sieves are mixed into the liquid base using both single blade turbine mixers and drum rolling techniques. The mixing is done under nitrogen blanket to prevent moisture pickup from the air. Total mix time is 2 hours, after which 0.1-0.4% of the moisture in the liquid base is removed. Molecular sieves are removed by passing the liquid base through a 20-30 mesh screen. Liquid base is returned to the mix tank..
- 4) Additional solid ingredients are prepared for addition to the composition. Such solid ingredients include the following:
  - Sodium carbonate (particle size 100 microns)
  - Sodium citrate anhydrous
  - Maleic-acrylic copolymer (BASF Sokolan)
  - Brightener (Tinopal PLC)
  - Tetra sodium salt of hydroxyethylidene diphosphonic acid (HEDP)
  - Sodium diethylene triamine penta methylene phosphonateThese solid materials, which are all millable, are added to the mix tank and mixed with the liquid base until smooth. This approximately 1 hour after addition

of the last powder. The tank is blanketed with nitrogen after addition of the powders. No particular order of addition for these powders is critical.

- 6) The batch is pumped once through a Fryma colloid mill, which is a simple rotor-stator configuration in which a high-speed rotor spins inside a stator which creates a zone of high shear. This reduces the particle size of all of the solids. This leads to an increase in yield value (i.e. structure). The batch is then recharged to the mix tank after cooling.
- 7) The bleach precursor particles are mixed with the ground suspension from the first mixing step in a second mixing step. This mixture is then subjected to wet grinding so that the average particle size of the bleach precursor is less than 600 microns, preferably between 50 and 500 microns, most preferred between 100 and 400 microns.
- 8) Other solid materials could be added after the first processing step. These include the following :  
Sodium percarbonate (400-600 microns)  
Protease, cellulase and amylase enzyme prills (400-800 microns)  
Titanium dioxide particles (5 microns)  
These non-millable solid materials are then added to the mix tank followed by liquid ingredients (perfume and silicone-based suds suppressor). The batch is then mixed for one hour (under nitrogen blanket). The resulting composition has the formula set forth in Table II.

**TABLE I**  
**Non-Aqueous Liquid Detergent Composition with Bleach**

<u>Component</u>	<u>Wt % Active</u>
*LAS Na Salt	21.7
C12-16EO=5 alcohol ethoxylate	18.98
BPP	18.98
Sodium citrate	1.42
[4-[N-nonanoyl-6-aminohexanoyloxy] benzene sulfonate] Na salt	7.34
DiEthyleneTriamine	0.90
PentaMethylenePhosphate Na salt	
Chloride salt of methyl quarternized polyethoxylated hexamethylene diamine	0.95
Sodium Carbonate	3
Maleic-acrylic copolymer	3.32
HEDP Na salt	0.90
Protease Prills	0.40
Amylase Prills	0.84
Cellulase Prills	0.5
Sodium Percarbonate	18.89
Suds Suppressor	0.35
Perfume	0.46
Titanium Dioxide	0.5
Brightener	<u>0.14</u>
Miscellaneous	100.00%

The resulting Table I composition is a stable, pourable anhydrous heavy-duty liquid laundry detergent which provides excellent stain and soil removal performance when used in normal fabric laundering operations.

\* LAS : alkylbenzene sulfonate sodium salt derived from alkylbenzenes having tetraline content lower than 5%.

WHAT IS CLAIMED IS:

1. A nonaqueous liquid detergent containing a surfactant selected from the alkali metal salts of C<sub>10</sub>-C<sub>16</sub> alkylbenzene sulfonic acid derived from alkylbenzenes having a tetraline content lower than 5%.
2. A nonaqueous liquid detergent composition according to claim 1 wherein said surfactant is sodium or potassium linear straight chain alkylbenzene sulfonate in which the average number of carbon atoms in the alkyl group is from 10 to 16 carbon atoms.
3. A nonaqueous liquid detergent composition according to claim 2 wherein the average number of carbon atoms in the alkyl group is from 11 to 14.
4. A nonaqueous liquid detergent composition according to claims 1-3 wherein said surfactant is sodium C<sub>11</sub>-C<sub>14</sub> linear alkylbenzene sulfonate.
5. A nonaqueous liquid detergent composition according to claims 1-4 wherein said surfactant comprises from 10% to 60% by weight of the composition.



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(74) Agents: REED, T., David et al.; The Procter & Gamble Company, 5299 Spring Grove Avenue, Cincinnati, OH 45217 (US).			
(54) Title: NONAQUEOUS DETERGENT COMPOSITIONS CONTAINING SPECIFIC ALKYL BENZENE SULFONATE SURFACTANT			
(57) Abstract <p>This invention relates to a nonaqueous liquid detergent containing a surfactant selected from the alkali metal salts of C<sub>10</sub>-C<sub>16</sub> alkylbenzene sulfonic acid derived from alkylbenzenes having a tetraline content lower than 5 %.</p>			

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# INTERNATIONAL SEARCH REPORT

International Application No

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A. CLASSIFICATION OF SUBJECT MATTER  
IPC 6 C11D17/00 C11D1/22

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C11D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 92 09678 A (S. B. CHEMICALS LIMITED ) 11 June 1992 cited in the application see claims 1-6 see page 5 - page 6 ---	1-5
A	EP 0 484 095 A (THE CLOROX CO. ) 6 May 1992 cited in the application see page 6, line 40 - line 57 see claims 1,8-11 ---	1-5
A	US 4 923 635 A (SIMION F. ANTHONY ET AL.) 8 May 1990 see column 3, line 53 - column 4, line 26 see claim 1 ---	1-5 -/-

Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

\* Special categories of cited documents :

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Date of the actual completion of the international search

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Serbetsoglou, A

## INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 97/10114

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